been observed under UHV conditions on the Ru(001) surface in transient thermal desorption experiments.[45] The lower reactivity of ruthenium and iron for the oxidation of carbon monoxide and hydrogen is a consequence of the stronger metal–oxygen bonds that are formed[6,46] compared with those of platinum[47] and palladium.[48]

Finally, the chemistry of ethylene on the Ru(001)–p(2×2)O surface may be compared to the organometallic chemistry of homogeneous compounds. For example, it has been shown that ethylene reacts with $Os_3(CO)_{12}$ to form the vinyl complex, $HOs_3(CH{=}CH_2)(CO)_{10}$, which forms the vinylidene complex, $H_2Os_3(CO)_9(C{=}CH_2)$[22] upon heating. The latter can be hydrogenated to an ethylidyne complex, $H_3Os_3(CO)_9(CCH_3)$,[22,25,49] just as chemisorbed vinylidene can be rehydrogenated to ethylidyne on the Ru(001)–p(2×2)O surface. These results also suggest that the conversion of π-bonded ethylene to vinylidene on Ru(001)–p(2×2)O occurs via a vinyl intermediate.

V. Conclusions

The presence of ordered p(2×2) and p(1×2) oxygen overlayers on the Ru(001) surface gives rise to π-bonding of molecularly chemisorbed ethylene, such that the carbon atoms of the ethylene remain nearly sp^2-hybridized. This species is qualitatively different from the sp^3-hybridized, di-σ-bonded ethylene that is observed on the clean surface. Intuitively, this difference reflects the greater Lewis acidity of the Ru(001)–p(2×2)O and Ru(001)–p(1×2)O surfaces. More precisely, it is a consequence of a significant perturbation in the electronic structure of the ruthenium surface by the ordered oxygen overlayers, which increases the energy separation between the Fermi level and the π^* orbital of ethylene, making back-donation unfavorable.

As observed on the oxygen-precovered Pt(111), Pd(100), and Fe(111) surfaces, a larger fraction [one-third on Ru(001)–p-(2×2)O] of π-bonded ethylene desorbs molecularly than does di-σ-bonded ethylene on the reduced surfaces. The remaining two-thirds of the saturation coverage of ethylene adsorbed on the Ru(001)–p(2×2)O surface dehydrogenates to ethylidyne probably via a vinylidene intermediate upon heating to 250 K. In contrast to the observed total decomposition of ethylidyne to carbon and hydrogen on the Ru(001) surface with no stable intermediates, the presence of oxygen induces the formation of an sp^2-hybridized vinylidene species from ethylidyne at 350 K. By analogy to the $H_2Os_3(CO)_9(CCH_2)$ cluster,[22,25,49] this chemisorbed vinylidene is almost certainly bridge-bonded to two adjacent ruthenium atoms and tilted toward a third ruthenium atom with donation of electron density from the π orbital to the d band of the ruthenium surface, as shown in Figure 5c. The chemisorbed vinylidene decomposes near 400 K to carbon adatoms and methylidyne, the latter of which dehydrogenates between 500 and 700 K. The vinylidene could be rehydrogenated to ethylidyne in the presence of hydrogen, analogous to the formation of ethylidyne from CCH_2 on reduced Pt(111) and Pd(111).[23,24] No oxygen-containing intermediates in ethylene decomposition were observed under any conditions of temperature and coverage. Oxygen adatoms reacted only with carbon adatoms, forming CO above 500 K.

Finally, the presence of oxygen favors η^1-bonding and sp^2 hybridization as shown by both the existence of π-bonded ethylene on the oxygen-precovered Pt(111), Pd(100), Fe(111), and Ru(001) surfaces,[8-11] as well as the formation of sp^2-hybridized vinylidene on these chemically modified Ru(001) and Pt(111) surfaces.[10] On the other hand, η^2-bonded, sp^3-hybridized ethylene was observed in the absence of oxygen on all four surfaces.

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Infrared Matrix Isolation Study of Hydrogen Bonds Involving C–H Bonds: Alkynes with Oxygen Bases

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Abstract: The hydrogen-bonded complexes of acetylene and a set of related alkynes with a series of oxygen-containing bases have been isolated in inert matrices at 14 K and characterized by infrared spectroscopy. Coordination of the acetylenic hydrogen to the oxygen atom of the base was evidenced by shifts of the C–H stretching mode, ν_s, to lower energies. These shifts, in the range of 50–100 cm^{-1}, were smaller than those observed previously for hydrogen-bonded complexes. Nonetheless, the shifts were distinct and variable with the different alkynes and bases employed, indicating the accessibility of a range of complexes. For example, the codeposition of propyne with $(CH_3)_2O$, $(CH_3)_2CO$, $(CH_2)_2O$, and $(CH)_4O$ gave rise to a perturbed C–H stretching mode shifted 71, 64, 55, and 16 cm^{-1} from the parent C–H stretching mode, respectively. The shifts for the substituted alkynes varied in the order phenylacetylene > *tert*-butylacetylene > 1-butyne > propyne, consistent with gas-phase acidity data.

Hydrogen bonding has been a subject of great interest to chemists over the years, as its importance to many areas of chemistry has long been recognized.[1] As a result of this interest, much study has been directed toward a more complete understanding of this very important molecular interaction. Despite much experimental effort and theoretical discussion, the details of hydrogen bonding are by no means completely understood.

The most frequent participants in hydrogen bonding are the highly electronegative elements N, O, and F, although elements of lesser electronegativity have been studied as well. The ability of group IVA elements to participate in hydrogen bonding, particularly carbon and silicon, has also generated substantial experimental and theoretical interest.[2-5] It is generally accepted

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that the hybridization of the carbon atom plays an important role in determining the effectiveness of the C–H group as a proton donor. The acidity of the carbon-bound hydrogen increases as the percent of s character on the carbon increases (i.e., sp > sp^2 > sp^3). The acidity of this hydrogen is also dependent on the substituents on the carbon atom.

In studies undertaken to further characterized the C–H group as a proton donor, Klemperer and co-workers[6-9] examined four relevant systems in supersonic expansions. The complexes of C_2H_2 and C_2H_4 with H_2O, and C_2H_2 of CF_3H with NH_3 were studied, and hydrogen bonding involving the C–H bond was noted in all but the C_2H_4/H_2O system. In addition, several groups have observed hydrogen bonding involving the C–H bond of HCN.[4,10,11] Finally, Barnes[12] has found evidence for C—H···N hydrogen bond formation between CF_3H and NH_3 in an argon matrix.

The matrix isolation technique[13-15] has been used repeatedly for the study of weakly bound complexes,[16-18] including hydrogen-bonded complexes.[19-23] Further, infrared spectroscopy has emerged as one of the most effective experimental tools for the study of hydrogen bonding interactions, in that hydrogen bond formation gives rise to distinct, readily identifiable spectral features.[1] Consequently, a study was undertaken to examine the interaction between acetylene and a series of related alkynes with several oxygen-containing bases after isolation in inert matrices.

Experimental Section

All of the experiments conducted in this study were carried out on a conventional matrix isolation system that has been described previously.[24] The gases employed here, C_2H_2, C_3H_4, $(CH_3)_2O$, and $(CH_2)_2O$ (all Matheson), were subjected to one or more freeze–thaw cycles at 77 K prior to sample preparation. Phenylacetylene (Aldrich), 1-butyne (Wiley Organics), *tert*-butylacetylene (Pfaltz and Bauer), acetone (Fisher), and furan, $(CH)_4O$ (Fisher), were introduced into the vacuum system via a glass finger and were also subjected to one or more freeze–thaw cycles. C_2D_2 and C_2HD were prepared by adding a mixture of D_2O and H_2O (approximately 4:1 ratio) to a vessel containing calcium carbide. The gaseous product passed through a drying column and was condensed at 77 K. The products were then purified by repeated freeze–thaw cycles. Argon and nitrogen were used as the matrix gases and were used without further purification.

The majority of the experiments were conducted in the twin jet mode, in which the two reactants, each diluted in the matrix gas, were codeposited from separate vacuum lines. A few experiments were also conducted in the single jet mode, for comparison. Deposition was carried out at roughly 2 mmol/h for 20–24 h from each line, before final spectra were recorded on a Perkin-Elmer 983 infrared spectrometer. Typically, 25–36 scans were averaged for the final high-resolution spectrum, with a resolution of 2.2 cm^{-1} at 1000 cm^{-1}. Normal coordinate calculations were carried out on the University of Cincinnati Amdahl system, using a program from the National Research Council of Canada, employing a valence force field.

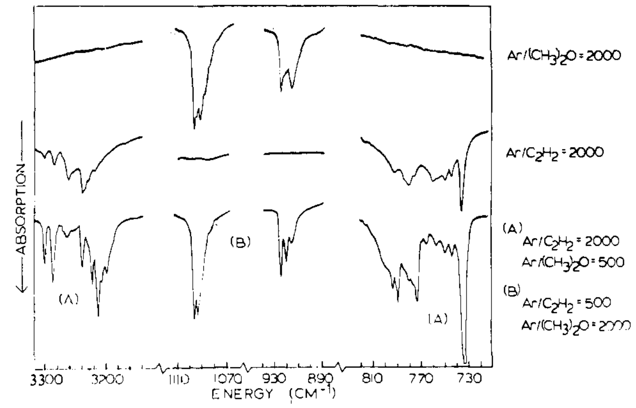

Figure 1. Infrared spectra of the sample arising from the codeposition of C_2H_2 and $(CH_3)_2O$ into argon matrices at two different concentrations (lower traces) compared to blank spectra of the reagents, over selected spectral regions.

Results

Prior to the codeposition of any of the reactants in this study, blank experiments were conducted on each at representative concentrations. In every case, the resulting spectrum was in good agreement with available literature spectra,[25-36] as well as with spectra previously recorded in this laboratory. Spectra of experiments involving C_2H_2 also contained bands at 784, 791, 1961, and 3238 cm^{-1}, which have been assigned by Engdahl and Nelander[37] to a complex between C_2H_2 and H_2O.

Acetylene, C_2H_2, Reactions. The twin jet codeposition of C_2H_2 with $(CH_3)_2O$, each at a concentration of 500/1 in argon, gave rise to intense new spectral features near 795 and 3200 cm^{-1}, with half-widths of 50–60 cm^{-1} (compared to widths of 5–6 cm^{-1} for the parent species). In addition, a weak new feature was observed at 1959 cm^{-1}, near the C–C stretching mode of $(C_2H_2)_2$ at 1965 cm^{-1}. Dilution of the base in argon to 2000/1 resulted in a substantial sharpening of the entire spectrum, allowing a more accurate determination of the bands reported above. In the C–H region, a distinct triplet was observed at 3196, 3212, and 3222 cm^{-1}, spanning 32 cm^{-1} at half-height. In the C–C–H bending region, a doublet was noted at 774 and 790 cm^{-1}, while near the intense parent modes of $(CH_3)_2O$ at 925 and 1094 cm^{-1} weak features were observed at 920 and 1091 cm^{-1}. In further experiments, the C_2H_2 concentrations were reduced and those of the base increased. The same set of product features was noted, with the central feature becoming relatively more dominant; the relative intensities of these bands to the absorptions of $(C_2H_2)_2$ increased systematically as the ratio of base-to-acetylene increased. Finally, single jet deposition of these two reactants gave identical results to those obtained in the twin jet mode. Figure 1 shows representative infrared spectra of matrices containing this pair of reactants.

$(CH_3)_2O$ was also codeposited with samples of partially deu-

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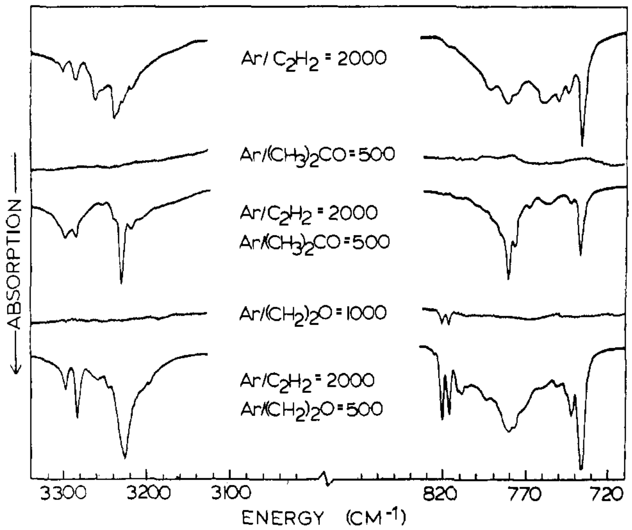

Figure 2. Infrared spectra obtained after codeposition of C_2H_2 and $(CH_3)_2CO$ into argon matrices (middle trace) and C_2H_2 with $(CH_2)_2O$ (bottom trace), compared to appropriate blank spectra.

teriated acetylene, with a D/H ratio of approximately 2, so that the ratio of species was roughly C_2D_2:C_2HD:C_2H_2 = 4:4:1. New product bands were observed in the C–H and C–D stretching regions at 2394, 2525, and 3238 cm^{-1}. In the low-energy region, severe overlap occurred between the monomers and dimers of the different isotopic species, and no distinct product bands could be resolved. This experiment was repeated at higher concentration, and the same set of product bands was observed, with the same relative intensities.

The twin jet deposition of acetylene with acetone at dilutions of $Ar/C_2H_2 = 2000$ and $Ar/(CH_3)_2CO = 500$ gave rise to new bands, with shifts and intensities comparable to those described above. A band of roughly 30 cm^{-1} half-width was noted at 3231 cm^{-1}, with shoulders at 3219 and 3242 cm^{-1}. A doublet was observed at 775 and 780 cm^{-1}, along with a quite weak feature at 1962 cm^{-1}. As the acetylene concentration was increased, and the acetone concentration decreased, the product bands became relatively less intense than the absorptions of parent C_2H_2. No new features were observed near parent $(CH_3)_2CO$ modes. Codeposition of acetone with partially deuteriated acetylene gave rise to distinct product absorptions in the C–D stretching region at 2405 and 2538 cm^{-1}, while in the C–H region a potential product band was observed at 3258 cm^{-1}. However, this band lies sufficiently close to a absorption of either $(C_2HD)_2$ or $(C_2HD)(C_2D_2)$ at 3261 cm^{-1} that it cannot be identified with certainty as a product band.

Acetylene and ethylene oxide were codeposited in the twin jet mode over a range of concentrations. New absorptions were noted at 3229 (half-width of 16 cm^{-1}), 779, 807, and 810 cm^{-1} as well as a very weak feature at 1961 cm^{-1}. Decreasing the concentration of C_2H_2 while keeping that of $(CH_2)_2O$ constant caused a decrease in the intensity of the above product bands. At the same time, the intensity of dimeric acetylene decreased more rapidly than did the product absorptions. Figure 2 shows infrared spectra of samples formed through the codeposition of C_2H_2 with $(CH_3)_2CO$ and with $(CH_2)_2O$.

The twin jet codeposition of samples of C_2H_2 at dilutions of 500/1 and 2000/1 in argon with samples of $(CH)_4O$ = 2000/1 and 500/1, respectively, led to production of a band at 3253 cm^{-1} (with a half width of 24 cm^{-1}), a doublet at 748, 751 cm^{-1}, and a weak band at 1964 cm^{-1}. These bands all increased in intensity relative to the parent C_2H_2 bands as the concentration of $(CH)_4O$ increased relative to that of C_2H_2.

Propyne, C_3H_4, Reactions. The codeposition of a sample of $Ar/C_3H_4 = 1000$ with a sample of $Ar/(CH_3)_2O = 500$ resulted in the appearance of a new absorption at 3249 cm^{-1}, with a half-width of 12 cm^{-1}. A very weak new absorption was observed at 2130 cm^{-1}, near the weak parent mode at 2136 cm^{-1}, as well as shoulders at 624 and 636 on the intense parent mode at 629 cm^{-1}; these new features are shown in Figure 3. Codeposition of propyne with acetone gave quite similar results: a broad absorption at 3256 cm^{-1}, a weak feature at 2131 cm^{-1}, and a shoulder at 624 cm^{-1}. A similar experiment involving C_3H_4 and $(CH_2)_2O$ gave rise to two new absorptions, at 2131 and 3265 cm^{-1}. Again, the 3265-cm^{-1} band was significantly broader than the corresponding parent mode at 3320 cm^{-1}. Finally, the codeposition of propyne with furan, $(CH)_4O$, resulted in the appearance of a broad, weak feature at 3304 cm^{-1}, with a shoulder at 3295 cm^{-1}. An increase in the concentration of furan, while holding that of propyne constant, led to a growth of the 3304-cm^{-1} product band relative to parent propyne absorptions.

***tert*-Butylacetylene, C_6H_{10}, Reactions.** The codeposition of a sample of $Ar/C_6H_{10} = 1000$ with a sample of $Ar/(CH_3)_2O = 500$ resulted in the formation of a weak, broad product absorption with maxima at 3236 and 3251 cm^{-1} and a half-width of approximately 35 cm^{-1}. Also, a decrease in intensity was noted for a weak band at 638 cm^{-1} relative to a blank experiment of C_6H_{10}. These same reactants were studied in a nitrogen matrix as well; a new absorption with a maximum at 3242 cm^{-1} and a shoulder at 3251 cm^{-1} was observed, while no distinct changes were noted in the low-energy region.

tert-Butylacetylene was also codeposited with acetone into an argon matrix and resulted in formation of weak absorptions at 3248 and 3271 cm^{-1}, as well as a decrease in the 638-cm^{-1} band relative to the blank spectrum of C_6H_{10}. Codeposition into an N_2 matrix led to quite similar results, with a weak, broad absorption centered at 3251 cm^{-1}. Finally, codeposition of C_6H_{10} with $(CH_2)_2O$ into an argon matrix gave rise to a weak, broad (24-cm^{-1} half-width) absorption, with maxima at 3250 and 3262 cm^{-1}. No distinct change was noted in the 638-cm^{-1} parent absorption.

1-Butyne, C_4H_6, Reactions. The codeposition of a sample of $Ar/C_4H_6 = 1000$ with a sample of $Ar/(CH_3)_2O = 500$ resulted in the formation a moderately broad (17-cm^{-1} half-width) absorption at 3240 cm^{-1}, as well as new very weak features at 3349 and 621 cm^{-1}. In addition, a decrease in intensity of a band at 643 cm^{-1} relative to a blank spectrum of C_4H_6 was observed. In a similar manner, 1-butyne was also codeposited with acetone; this led to the formation of a broad, weak absorption with half-width of 36 cm^{-1} and maxima at 3246, 3262, and 3275 cm^{-1}. In addition, a weak feature was observed at 617 cm^{-1}, along with a decrease in the absorption at 643 cm^{-1}. At more dilute concentrations, all of these absorptions decreased in intensity, to the point where observation of the broad feature at high energies was difficult.

Phenylacetylene, C_6H_6, Reactions. This alkyne was codeposited with dimethyl ether into an argon matrix, which resulted in the formation of a broad absorption, with half-width of 25 cm^{-1} and maxima at 3223 and 3236 cm^{-1}. A shift in the relative intensities of the parent doublet at 2120 and 2124 cm^{-1} was noted, with the 2120-cm^{-1} band becoming relatively more intense in the presence of $(CH_3)_2O$. In addition, a weak new feature was observed at 620 cm^{-1}, as well as a shoulder at 658 cm^{-1} on the parent absorption near 646 cm^{-1}. C_8H_6 was also codeposited with $(CH_3)_2CO$ into an argon matrix: this led to formation of a major product absorption with maxima at 3238 and 3262 cm^{-1}. In addition, the same shift in intensities of the 2120- and 2124-cm^{-1} parent doublet was noted, with the band at 2120 cm^{-1} growing relative to the 2124-cm^{-1} band. In the low region, shoulders were noted at 621 and 658 cm^{-1} on the parent doublet at 610 and 646 cm^{-1}.

Table I summarizes product band positions in the upper, C–H stretching region for all of the systems described above.

Discussion

The codeposition of the alkynes employed here with oxygen-containing bases clearly resulted in new infrared absorptions which could not be ascribed to either of the isolated parent species. The observed product bands can be grouped into four sets: (1) those that occur near and to the red of the alkyne C–H stretching mode

Table I. Product Band Positions (cm^{-1}) and Shifts for the 1:1 Molecular Complexes of Alkynes with Oxygen-Containing Bases

	acid										
	C_2H_2		C_3H_4		C_4H_6		C_6H_{10}		C_8H_6		
base	ν_{CH}	$\Delta\nu$	ν_{CH}	$\Delta\nu$	ν_{CH}	$\Delta\nu$	ν_{CH}	$\Delta\nu$	ν_{CH}	$\Delta\nu$	PA^{b}
	3300		3320		3327		3327		3337		
$(CH_3)_2O$	3212	88	3249	71	3240	87	3244^{a}	83	3229^{a}	108	192
$(CH_3)_2CO$	3231	69	3256	64	3262^{a}	65	3248	79	3250^{a}	87	197
$(CH_2)_2O$	3229	71	3265	55			3256^{a}	71			188
$(CH)_4O$	3253	47	3304	16							192

^{a}Mean value. ^{b}Proton affinity of the base, in kcal/mol.

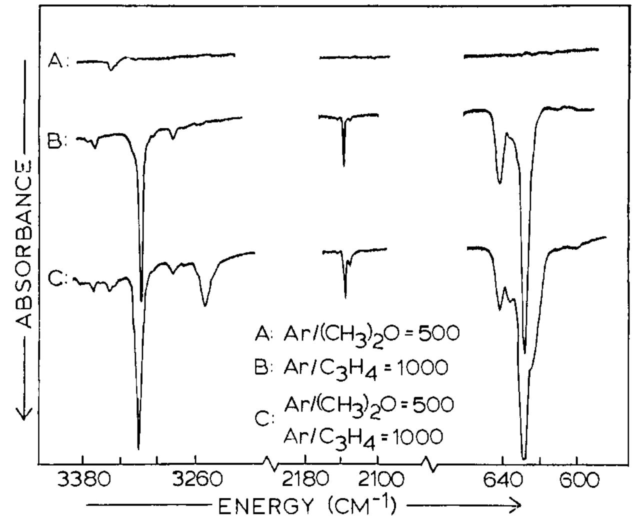

Figure 3. Infrared spectrum of the sample formed through the codeposition of propyne with dimethyl ether (trace C) compared to blank spectra of each reactant alone (traces A and B).

(3200–3400 cm^{-1}); (2) those near the parent C–C–H bending region (600–800 cm^{-1}); (3) those appearing in the spectral region corresponding to the carbon–carbon triple bond stretch (1950–2150 cm^{-1}); and (4) in some systems, those appearing near vibrational modes of the base. The location of all of the product bands is suggestive of slightly perturbed alkyne and base subunits rather than addition or rearrangement products. In addition, the intensity of all of these bands was directly proportional to the concentration of the alkyne and base employed (in the case of C_2H_2 with $(CH_3)_2O$ a product triplet was observed; however, at very high dilutions of both base and acetylene, the central component of the triplet became relatively dominant and was used for calculations). Consequently, the spectral data strongly indicate formation of a molecular complex, and the concentration data support assignment to a 1:1 complex between the alkyne and base subunits. At the concentrations employed, formation of higher aggregates (i.e., 2:1 complexes and so forth) is unlikely, with the possible exception of the C_2H_2 system. Here, at high C_2H_2 concentrations, shoulders were seen on the main product absorption in the C–H stretching region, which might be assigned to the complex of the base subunit with the acetylene dimer. However, the major product bands, which persisted at high dilutions, can confidently be assigned to a 1:1 complex.

For each system, the most distinctive spectral feature was the product absorption to lower energies of the parent C–H shift. This band was quite broad, and in a number of systems quite intense. These are precisely the infrared spectral characteristics of hydrogen bonding[1] and suggest that the complexes formed here are hydrogen bonded, involving the acetylenic hydrogen. It should be noted that the shifts observed here of roughly 50–100 cm^{-1} are substantially smaller than those observed for many other hydrogen-bonded systems.[19–23] Since the magnitude of the shift of ν_s is often correlated with the strength of interaction, the data obtained here indicate that the complexes are quite weakly bound. At the same time, shifts observed here were consistently larger than observed for the acetylene dimer,[36] indicating a stronger interaction with oxygen bases. This is supported by the observation that the intensity of the C_2H_2 dimer absorptions decreased in experiments in which the oxygen base was present, compared to blank experiments of the alkyne at the same concentration. Overall, the spectra demonstrate that a distinct, specific hydrogen-bonding interaction occurs in these complexes.

The deuterium results support this conclusion as well. When partially deuteriated acetylene was employed, the product absorptions in the upper region shifted strongly to lower energy, confirming that they may be assigned as above to the C–H (C–D) stretching mode. For the complex of C_2D_2 with $(CH_3)_2O$, the perturbed C–D stretch was noted at 2394 cm^{-1}, shifted down from the parent at 2441 cm^{-1}. When C_2HD was employed, both the H-bonded and D-bonded forms were observed, the former absorbing at 3238 cm^{-1} and the latter at 2525 cm^{-1}. Judging by relative intensities, the D-bonded form was formed somewhat preferentially over the H-bonded form, in agreement with work by Nelander on complexes of HOD.

The $C_2H_2{\cdot}(CH_3)_2O$ system provided both highest product yield (as judged by band intensities) and the strongest interaction (as judged by shift of ν_s). For this system, perturbed modes of the base subunit were observed as well, at 920 and 1091 cm^{-1}. These lie quite near the symmetric and antisymmetric C–O–C stretching modes of parent dimethyl ether,[25] respectively, and are so assigned to the perturbed base unit in the 1:1 complex. The fact that these two modes were most sensitive to complexes, as they have been with Lewis acids,[16,17,38] suggests that the site of complexation is to the oxygen atom of the base subunit, further supporting hydrogen bond formation.

An additional criterion for hydrogen bond formation is a shift to higher energies of the C–C–H bending mode, although this shift is typically substantially less than the shift of the C–H stretching mode. For all of the C_2H_2 complexes studied here, this bending mode was indeed detected, between 750 and 800 cm^{-1}. Further, since the symmetry of the acetylene subunit is lowered upon complex formation a splitting of the degeneracy of this parent mode is anticipated. For most of the C_2H_2 complexes studied, a doublet was observed, as anticipated. However, this region is sufficiently cluttered with dimeric C_2H_2 and the $C_2H_2{\cdot}H_2O$ complex that both components of the doublet were not observed in every case. For the remaining alkyne complexes, shoulders were often observed on the C–C–H bending mode absorption of the parent (such as the shoulders at 621 and 658 cm^{-1} on the parent absorptions at 610 and 646 cm^{-1} for the complexes of phenylacetylene). While not as clearly resolved, these shoulders were distinct and can be attributed to perturbed C–C–H bending modes for the appropriate complexes.

For any complex of C_2H_2, activation of the infrared inactive carbon–carbon stretch is anticipated (this mode is weakly activated for the acetylene dimer). For each complex of C_2H_2 a weak band was observed near 1960 cm^{-1}, to the red of the forbidden mode of parent C_2H_2 at 1974 cm^{-1} (gas-phase value, from Raman spectra), and just to the red of the absorption of $(C_2H_2)_2$ at 1965 cm^{-1}. For several of the large alkynes, weak features were observed in the carbon–carbon triple bond stretching region, all of which can be assigned to this mode in the hydrogen-bonded alkyne. Given the weakness of the interaction, only a slight activation was observed, and consequently a very low intensity.

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(38) Machara, N. P.; Ault, B. S. *Inorg. Chem.* **1985**, *24*, 4251.

While the magnitude of the shift of ν_s was quite small, the shift did vary noticeably with the different alkynes and bases employed. For the two bases which were complexed to each of the alkynes studied, $(CH_3)_2O$ and $(CH_3)_2CO$, the greatest shifts occurred with phenylacetylene, and the least with propyne. If the results for C_2H_2 are omitted for the moment (see below), the results for the remaining alkynes generally agree with the gas-phase acidities of these species, as determined by Bartmess and co-workers.[39] These researchers measured the free energy change for the reaction $AH(g) \rightarrow A^-(g) + H^+(g)$ which reflects the absolute acidity of the AH species. Their order of acidity matches the ordering of the magnitude of shift observed here for the acetone complexes, with the exception of the C_2H_2 complex (which should fall between phenylacetylene and *tert*-butylacetylene).

The magnitude of ν_s also varied with the particular base employed, as might be anticipated for the range of bases studied. In all cases, alkyne complexes with $(CH_3)_2O$ showed the greatest shifts, while complexes of $(CH)_4O$ consistently produced the smallest shifts. Intermediate values were obtained for the complexes with $(CH_3)_2CO$ and $(CH_2)_2O$, although band breadth and presence of submaxima made measurement of precise values for ν_s difficult. Most commonly, magnitude of shift is correlated[16,22,40] with the gas-phase basicity of the species, as measured by proton affinities.[41] Such correlations are not particularly useful here; for example, the proton affinity of $(CH_3)_2CO$ is greater than that of $(CH_3)_2O$, yet complexes of acetone with alkynes showed consistently smaller shifts. Barnes[22] and Morokuma[42] have noted that such a correlation does not exist for a wide range of more strongly hydrogen-bonded complexes, since there are several energetic terms comprising the interaction, and the proton affinity is only a partial measure of these. Further, the interactions here are quite weak and more susceptible to minor perturbations, including lattice packing arrangements. Consequently, an imperfect correlation with proton affinity is not particularly surprising, when the proton affinities are quite close in value. At the same time, results obtained in nitrogen matrices were quite similar to those in argon, with just slight shifts and changes in band contours. This indicates that lattice packing forces do not cause a major perturbation to these complexes. Also, preliminary results[43] with significantly stronger bases have shown distinctly larger shifts for ν_s.

As noted above, shifts for complexes of C_2H_2 do not fit the trends observed for remaining alkynes. Among the alkynes studied, C_2H_2 is unique in possessing (in the parent) two equivalent C–H bonds. These, then, are necessarily coupled, giving rise to a symmetric and an antisymmetric C–H stretching mode. Upon hydrogen bond formation, the equivalence is lost. However, in the limit of weak interaction, strong coupling will still remain between the two C–H bonds, in that their resonance frequencies would be very similar, although no longer identical. While the magnitude of the coupling is not known, it will in general affect the shift of ν_s (hydrogen bond formation will also weakly activate the symmetric C–H stretching mode). By comparison, the remaining alkynes have a massive substituent on the second carbon, leaving the lone C–H bond as an effectively isolated vibration. Consequently, the C_2H_2 complexes observed here are not directly comparable to those of the remaining alkynes studied.

The results of partial deuteriation support this conclusion as well. When C_2HD was employed, the C–H and C–D stretching modes are nearly completely decoupled. The shift of C–H stretching mode of C_2HD in its complex with either dimethyl ether or acetone was approximately 11% greater than the shift of the C–H stretching mode of C_2H_2 with the same base. This suggests that in the absence of coupling, the shift of the isolated C–H bond would have been somewhat greater, which would make the C_2H_2 data more in line with the remaining alkynes.

Normal coordinate calculations were carried out to support this point as well. A force field for C_2H_2 was refined to the known experimental frequencies (including the symmetric modes from gas-phase Raman data). One C–H bond was then perturbed, by lowering its force constant in increments of 0.10 mdyn/Å, and the shift of the C–H stretching modes recorded. A nonlinear relationship was observed between shift and degree of perturbation, for small perturbations, as anticipated due to coupling. The same procedure was then carried out for C_2HD, perturbing the C–H bond. A linear relationship was observed between shift and degree of perturbation, for a lowering of the C–H force constant of up to 0.6 mdyn/Å (which produced a shift of 170 cm^{-1}, which in turn is greater than the experimental shift). The nonlinearity observed for C_2H_2 is due to coupling of the two C–H oscillators; this plot did become linear for large perturbations, when the coupling was nearly completely destroyed. All of these arguments support the conclusion that the C_2H_2 data do not fit with the remaining alkynes as a consequence of coupling between the two nearly equivalent C–H oscillators.

Complexes of C_2H_2 and C_3H_4 have been studied with Lewis and Brønsted acids as well.[44-49] For these systems, complexation occurs to the π-electron density of the triple bond, in a perpendicular fashion. These studies have shown that the methyl group is a weak electron donor, leading to increased π-electron density, and strong interactions with acids. One might anticipate a lessening of the acidity of the acetylenic hydrogen by such electron donation (just as the π-basicity is increased). This is precisely the result observed here, with distinctly smaller shifts for the propyne complexes studied than the corresponding C_2H_2 complexes.

The apparent yield of product varied with the alkyne and base employed as well, as indicated by the intensity of ν_s. This is not surprising, given the substantial steric requirements for reaction with the larger, more complex alkynes and bases. Certainly, the greatest intensity of ν_s was consistently noted with C_2H_2, where there is minimal steric interference, and two acetylenic hydrogens are available for interaction. At the same time, the use of intensities of ν_s to measure yield is somewhat risky, in that absolute absorption coefficents are not known (the degree of intensification of ν_s is also dependent on the strength of interaction). In addition, the breadth of many of the C–H stretching modes for many of the complexes was sufficiently great that determination of the integrated intensity was difficult. The spectra, nonetheless, suggest that significantly more product was formed in the C_2H_2 experiments than with the remaining alkynes.

Summary

Hydrogen-bonded complexes of acetylene and related alkynes with oxygen-containing bases have been isolated and characterized in argon matrices. The observed shifts of the ν_s mode of the alkyne were small, but distinct and variable with the different acids and bases employed. For all of the alkynes, the largest shifts were noted with $(CH_3)_2O$, with $(CH)_4O$ producing the smallest shifts. For the substituted alkynes, the observed trend in ν_s with a reference base correlates well with known gas-phase acidities, with phenylacetylene yielding the greatest shift, and propyne the least. However, acetylene itself did not fit into this trend, likely as a consequence of the coupling between the two C–H bonds.

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